



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/SE92/00042 (22) International Filing Date: 24 January 1992 (24.01.92) (30) Priority data: 9100227-9 25 January 1991 (25.01.91) SE (71) Applicant: SANDVIK AB [SE/SE]; S-811 81 Sandviken (SE). (72) Inventor: GALLI, Enrico ; Mikkeltorg Allé 100, DK-2980 Kokkedal (DK). (74) Agent: TÅQUIST, Lennart; Patent Department, Sandvik AB, S-811 81 Sandviken (SE).		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), NO, RU, SE (European patent). Published <i>With international search report.</i>
(54) Title: CORROSION RESISTANT CEMENTED CARBIDE (57) Abstract The present invention discloses a sintered cemented carbide alloy with excellent corrosion and oxidation resistance. The alloy comprises 70-98 weight-% hard material essentially comprising WC in a monophase binderphase. It has surprisingly been found that by the use of submicron WC the corrosion and oxidation resistance can be improved compared to known corrosion and oxidation resistant cemented carbide alloys.		

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Corrosion resistant cemented carbide

5 The present invention relates to a new cemented carbide grade with excellent properties especially for tools in the wood industry. More particularly, the invention relates to a cemented carbide in which submicron WC has been distributed in a monophase binder phase based on Ni, Co and Cr.

10 Reconstituted wood products, such as medium density fibreboard and chipboard, are the main raw materials in the furniture industry. They are also used in the housing industry to some extent.

15 These products are machined with a variety of tool materials, from high speed steels to cemented carbide to polycrystalline diamond. A leading role has been played and is still being played by tools made with
20 cemented carbides.

The composition of the cemented carbide grades used for wood working tools consists generally of tungsten carbide (WC), as the hard component, and cobalt (Co) as
25 a binder to hold together the WC crystals. Sometimes small amounts of other carbides, like titanium carbide, tantalum carbide, etc, are added.

30 To satisfy the different demands on hardness and toughness, the amount of Co and/or the grain size of the WC are varied. Higher Co-content and/or larger grain size decrease hardness and increase toughness.

Mechanical wear, especially abrasion, has been thought
35 to be the primary mechanism of tool wear when machining

reconstituted wood products. Recent work, however, has proven that chemical mechanisms such as corrosion and oxidation play a significant role in tool degradation. The same is valid also for tools for machining of
5 printed circuit boards and similar composite materials.

As these wood products are machined, the tool temperature can increase dramatically. As the temperature increases, the wood products go through thermal break-
10 down resulting in the introduction of numerous chemicals into the cutting environment. In all, up to 213 different compounds have been identified upon the destructive distillation of wood. The machining of medium density fibreboard and particle board produces
15 even more decomposition products. These products not only have the wood fibres, but also a binder such as urea, formaldehyde, wax and glue fillers and extenders, and possibly chemicals added as flame retardants.

20 The decomposition products formed are highly corrosive and attack the Co-binder that holds the WC grains together. When this occurs, the WC grains are removed by mechanical action and the tool cutting edge loses its sharpness and its cutting capability.

25 The high temperature achieved when machining wood products contributes also to the degradation of the binder by oxidation of the Co in air.

30 What has been said above is also valid when cutting green lumber or dried wood. Both products contain moisture and organic acids capable of dissolving the Co-binder and therefore weakening the bond holding the carbide particles in place until the exposed particles
35 are removed mechanically.

The present invention relates to new types of cemented carbide with excellent properties regarding corrosion and oxidation resistance particularly satisfying the different needs of the wood industry. The other properties distinctive of cemented carbides, like resistance to abrasion, toughness and brazability, have been kept to an optimum.

Resistance to corrosion and oxidation has been achieved by alloying the binder and distribute it in a cemented carbide structure consisting of submicron WC-grains, which permit an optimal distribution of the binder, resulting in a structure consisting of both thin layers of binder and small WC grains. The large surface to volume ratio of the submicron WC grains permits an optimal anchorage of the grains to the binder.

The material according to the invention comprises 70-98 weight-% hard material which is essentially WC with a mean grain size smaller than $0.9\ \mu\text{m}$, preferably smaller than $0.7\ \mu\text{m}$, most preferably smaller than $0.5\ \mu\text{m}$. In addition, the material contains max 0.8 preferably max 0.2 weight-% of VC and/or ZrN. The binder phase comprises in solution, in weight-%, Co max 90, Ni max 90, Cr 3-15, W max 30, Mo max 15 and, in addition Al max 2, Mn max 10, Si max 2, Cu max 10, Fe max 20, Ag max 5 and Au max 10. In a preferred embodiment the Ni-based binder-phase comprises in solution, in weight-%, Co max 30 and Mo 1-6. In another preferred embodiment the binder-phase comprises in solution, in weight-%, Co 30-70 and Mo 1-6. The binder-phase may also comprise in solution 0.1-10 weight-% TiN and/or TiCN.

The concentration of carbon in the sintered cemented carbide must be kept within a narrow interval. This condition must be fulfilled in order to obtain a mono-

phase binder and to prevent the formation of brittle carbides. The optimal concentration of carbon to retain high resistance to corrosion and oxidation as well as toughness, must be, in percentage by weight, 6,13-
5 $(0,061 \pm A) \times (100 - \text{hard material in weight\%})$ for concentration of Cr+Mo between 3-15 weight-% where
A= 0.008, preferably A= 0.005 and 6,13- $(0,058 \pm B) \times$
(100-hard materials in weight %) for concentration of Cr+Mo between 16-30 weight-% where B= 0.007 preferably
10 B= 0.005.

The cemented carbide alloys according to the invention are manufactured by powder metallurgical methods: milling, pressing and sintering. The grain size of the
15 WC-powder shall be $< 0.8 \mu\text{m}$, preferably $< 0.6 \mu\text{m}$. By the addition of small amounts of VC and/or ZrN the WC-grain growth during sintering is inhibited.

The cemented carbide according to the invention is
20 particularly useful for cutting of chipboard, medium density fibreboard, particle board and solid dried and wet wood. For cutting of chipboard, medium density fibreboard and particle board the binder phase content shall be max 4 weight-% preferably max 3 weight-%, for
25 cutting of solid dried wood the binder phase content shall be 4-9 weight-%, preferably 4-6 weight-%, and for cutting of solid wet wood the binder phase content shall be 10-30 weight-%.

30 The cemented carbide according to the invention is also useful for tools such as drills, microdrills and routers for machining of printed electronic circuit boards and similar composite materials. In this application the binder content shall be 3-20, preferably 4-
35 12 weight-%.

Example

A cemented carbide grade according to the invention with the following composition in weight-%: Co 1.9, Ni 0.7, Cr 0.3, VC 0.2 and balance WC with a mean grain size of 0.6 μm was tested against a corrosion and oxidation resistant WC-Ni-Cr-Mo-alloy disclosed in e.g. EP-A-28620, see particularly ex 7 and a straight WC-Co-material both with the same binder-phase content. In the test, chipboard 20 mm covered on both sides with a 0.16 mm layer of melamine has been machined using a milling cutter and the following cutting data:

- diameter of cutter 125 mm
- cutting depth 3 mm
- cutting speed 40 m/s
- feed 6 m/min
- cutting edge angle 55
- rake angle 20
- clearance angle 15

The edge wear of the cutting edge as well as the surface finish of the chipboard were measured at 0, 2000, 5000, 20000 and 40000 meters.

The following results were obtained:

Average wear in μm at different cutting lengths, m

	2000	5000	20000	40000
According to the invention	25	37	73	87
WC+Ni+Cr+Mo	36	54	90	104
WC+Co	42	56	106	141

The cemented carbide according to the invention shows significantly lower wear than the conventional carbides. The conventional type of corrosion and oxidation resistant cemented carbide shows at 20000 meters about the same wear as the new type at 40000 meters.

The surface finish produced by the inserts of the straight WC-Co cemented carbide was found unacceptable after 20000 meters, while for the inserts in the new type of cemented carbide the surface finish was still acceptable after 40000 meters.

Claims

1. Sintered cemented carbide alloy with improved corrosion and oxidation resistance comprising 70-98 weight-% hard material comprising WC in a monophase binder-phase based on Ni and/or Co characterized in

that said binder-phase comprises in solution, in weight-%, Co max 90, Ni max 90, Cr 3-15, W max 30, Mo max 15,

that the total carbon content, in weight-%, is $6.13 - (0.061 \pm A) \times (100 - \text{hard material in weight-\%})$ for concentrations of Mo+Cr between 3 and 15 weight-% where $A = 0.008$, preferably $A = 0.005$ and $6.13 - (0.058 \pm B) \times (100 - \text{hard material in weight-\%})$ for concentrations of Mo+Cr between 16 and 30 weight-% where $B = 0.007$, preferably $B = 0.005$

that the mean grain size of WC is <0.9 , preferably $<0.7 \mu\text{m}$

and that the alloy further contains <0.8 , preferably $<0.2\%$ VC and/or ZrN.

2. Sintered cemented carbide alloy according to claim 1 characterized in that said binder-phase comprises in solution, in weight-%, Co max 30 and Mo 1-6.

3. Sintered cemented carbide alloy according to claim 1 characterized in that said binder-phase comprises in solution, in weight-%, Co 30-70 and Mo 1-6.

4. Sintered cemented carbide alloy according to any of the preceding claims characterized in that said binder-phase further comprises in solution, in weight-%, Al max 2, Mn max 10, Si max 2, Cu max 10, Fe max 20, Ag max 5 and Au max 10.
5. Sintered cemented carbide alloy according to any of the preceding claims characterized in that said binder-phase comprises in solution 0.1-10 weight-% TiN and/or TiCN.
6. Use of the sintered cemented carbide alloy according to any of the preceding claims with a binder-phase content of max 4 weight-% for cutting of chipboard, medium density fibreboard and particle board.
7. Use of the sintered cemented carbide alloy according to any of claims 1-5 with a binder-phase content of 4-9 weight-% for cutting of solid dried wood.
8. Use of the sintered cemented carbide alloy according to any of claims 1-5 with a binder-phase content of 10-30 weight-% for cutting of solid wet wood.
9. Use of the sintered cemented carbide alloy according to any of claims 1-5 with a binder-phase content of 3-20 weight-% in tools for machining of printed electronic circuit boards and similar composite materials.

INTERNATIONAL SEARCH REPORT

International Application No **PCT/SE 92/00042**

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 22 C 29/08														
II. FIELDS SEARCHED <div style="text-align: right; margin-right: 100px;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 25%; border: none;">Classification System</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: none; height: 40px; vertical-align: bottom;">IPC5</td> <td style="border: none; vertical-align: bottom;">C 22 C</td> </tr> </table> <div style="text-align: center; margin-top: 10px; font-size: small;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in Fields Searched⁸</div>			Classification System	Classification Symbols	IPC5	C 22 C								
Classification System	Classification Symbols													
IPC5	C 22 C													
SE,DK,FI,NO classes as above														
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category *</th> <th style="width: 60%;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 30%;">Relevant to Claim No.¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X A</td> <td style="vertical-align: top;">WO, A1, 8002569 (SANDVIK AKTIEBOLAG) 27 November 1980, see page 5, line 1 - page 7, line 34; page 22, line 35 - page 27, line 4 --</td> <td style="vertical-align: top; text-align: center;">1-4,6-9 5</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X A</td> <td style="vertical-align: top;">Patent Abstracts of Japan, Vol 9, No 293, C315, abstract of JP 60-135552, publ 1985-07-18 (TOSHIBA TUNGALOY K.K.) --</td> <td style="vertical-align: top; text-align: center;">1-5 6-9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X A</td> <td style="vertical-align: top;">EP, A2, 0195965 (FRIED. KRUPP GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG) 1 October 1986, see page 2, line 5 - line 16; page 3, line 21 - page 2, line 23 --</td> <td style="vertical-align: top; text-align: center;">1 2-9</td> </tr> </tbody> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X A	WO, A1, 8002569 (SANDVIK AKTIEBOLAG) 27 November 1980, see page 5, line 1 - page 7, line 34; page 22, line 35 - page 27, line 4 --	1-4,6-9 5	X A	Patent Abstracts of Japan, Vol 9, No 293, C315, abstract of JP 60-135552, publ 1985-07-18 (TOSHIBA TUNGALOY K.K.) --	1-5 6-9	X A	EP, A2, 0195965 (FRIED. KRUPP GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG) 1 October 1986, see page 2, line 5 - line 16; page 3, line 21 - page 2, line 23 --	1 2-9
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<div style="display: flex; justify-content: space-between; font-size: x-small;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>														
IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> <div style="border: 1px solid black; padding: 5px; margin-bottom: 5px;"> Date of the Actual Completion of the International Search 21st April 1992 </div> <div style="border: 1px solid black; padding: 5px;"> International Searching Authority <div style="text-align: center; margin-top: 10px;">SWEDISH PATENT OFFICE</div> </div> </td> <td style="width: 50%; border: none; vertical-align: top;"> <div style="border: 1px solid black; padding: 5px; margin-bottom: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center; margin-top: 10px;">1992 -04- 27</div> </div> <div style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center; margin-top: 10px;"> Nils Engnell </div> </div> </td> </tr> </table>			<div style="border: 1px solid black; padding: 5px; margin-bottom: 5px;"> Date of the Actual Completion of the International Search 21st April 1992 </div> <div style="border: 1px solid black; padding: 5px;"> International Searching Authority <div style="text-align: center; margin-top: 10px;">SWEDISH PATENT OFFICE</div> </div>	<div style="border: 1px solid black; padding: 5px; margin-bottom: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center; margin-top: 10px;">1992 -04- 27</div> </div> <div style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center; margin-top: 10px;"> Nils Engnell </div> </div>										
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		Relevant to Claim No
Category	Citation of Document, with indication, where appropriate, of the relevant passages	
X	US, A, 4950328 (NIRO ODANI ET AL) 21 August 1990, see column 1, line 1 - column 2, line 46 table 1	1
A	--	2-9
A	EP, A1, 0214679 (METALLWERK PLANSEE GESELLSCHAFT M.B.H.) 18 March 1987, see column 2, line 41 - line 54; column 9, line 11 - column 10, line 57	1-9
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A	Patent Abstracts of Japan, Vol 10, No 245, C368, abstract of JP 61- 76645, publ 1986-04-19 (MITSUBISHI METAL CORP)	1-9
A	Patent Abstracts of Japan, Vol 10, No 245, C368, abstract of JP 61- 76646, publ 1986-04-19 (MITSUBISHI METAL CORP)	1-9
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	Patent Abstracts of Japan, Vol 13, No 241, C604, abstract of JP 01- 52043, publ 1989-02-28 (NACHI FUJIKOSHI CORP) ----- -----	1-9

ANNEX TO THE INTERNATIONAL SEARCH REPORT **ON INTERNATIONAL PATENT APPLICATION NO. PCT/SE 92/00042**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 28/02/92. The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 8002569	80-11-27	AT-E- 9169	84-09-15
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		SE-A- 7904331	80-11-18
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